

Influence of chirality on phase behaviour of side chain liquid crystalline polymers

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Summary

Two kinds of chiral side chain liquid crystalline polyacrylates were synthesized and characterized by DSC, POM and x-ray diffraction. The results indicated that chirality of side chain end group and spacer length strongly influence the phase behaviour of the polymers. The polymer P-I with one asymmetric carbon atom of end group exhibits enantitropic Smectic S_A and S_C^* phases. The polymer P-III having two asymmetric carbon atoms displays enantitropic Smectic S_A and S_B phases. Formation of liquid crystalline polymorphism of polymers depends on spacer length of side chains.

Introduction

Recently, ferroelectric liquid crystalline polymers have attracted a good deal of attraction from the viewpoint of basic liquid crystalline science and its potential application.^[1-2] But the mutual interaction of molecular structure and mesophase behaviour is not well understood. In order to define the contribution of the chiral end group to the liquid crystalline polymers, two kinds of chiral side chain polyacrylates were synthesized and investigated by DSC, POM and x-ray diffraction. The effects of chirality of end group and spacer length of side chain on the phase behaviour exhibited by synthesized polymers are discussed.

Experimental

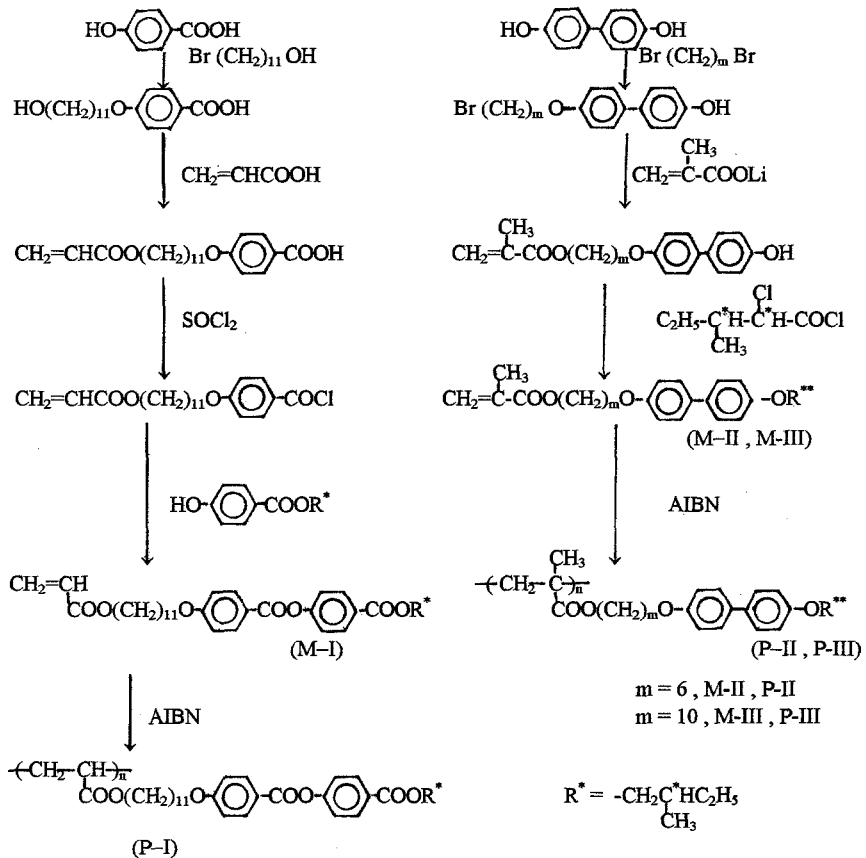
The scheme 1 shows the synthesis of monomers and polymerization reaction.

Synthesis routes of monomers was shown in reference [3]. The structure of the monomers were confirmed by $^1\text{H-NMR}$ on JEOLJNM-FX 100 NMR spectrometer and elemental analysis. The characterization of monomers is given in Tab.1.

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Tab.1 Characterization of monomers

Monomers	Elemental Analysis				Transition Temperature (°C)	Yield (%)
	Found		Calc.			
	(C%)	(H%)	(C%)	(H%)		
M - I	70.0	8.02	71.7	8.07	K 29.8 S _A 37.3 I	43
M - II	74.55	7.39	75.14	7.38	-	~30
M - III	76.06	8.34	75.58	8.15	K 50.2 I	~30



Scheme 1

Polymers were prepared by free radical initiation (AIBN 1 mole% vs monomers) solution polymerization reaction in THF solvent at 60°C for 48hr, then the polymers were precipitated by addition of methanol to the reaction solution.

Molecular weight of the polymers were determined by Waters R401 liquid chromatography, polystyrene as the standard. Thermal transition was determined by using a Perking-Elmer DSC-7 differential scanning calorimeter, heating and cooling rates were 20°C/min. In order to erase thermal history, thermal transition data were collected during the second heating and cooling scan, an Olympus BH-2 optical polarized microscope (POM) equipped with a Mettler FP5 hot stage was used to observe the anisotropic texture. X-ray diffraction measurements were performed by Guinier-type focusing camera with a bent quartz monochromator (CuK α as radiation) at 20-100°C or SIEMENS D-500 diffractometer with FeK α as radiation source at room temperature.

Results and Discussion

Tab.1 shows the phase transition temperatures of monomers. Monomer M-I exhibits a melting transition at 29.8°C, a Smectic S_A to isotropic transition at 39°C. However, M-II and M-III don't display liquid crystalline property. M-III only shows melting transition at 50°C.

The number average molecular weight of polymers is in the range of 5×10^3 - 3×10^4 . Characterization of polymers is listed in Tab.2. Polymers P-I and P-III having longer spacer present Smectic polymorphism. DSC curves of the polymers are presented in Fig.1. Polymer P-I exhibits an enantitropic Smectic S_A and Smectic S_C^{*} phases. P-III exhibits an enantitropic Smectic S_A and Smectic S_B phases. The phase assignment was conducted by optical polarized microscopic observation and x-ray diffraction measurements. Fig.2 shows the photographs of texture of polymer P-I. A focal conic smectic texture reveals at 67°C (Fig.2 a). When temperature was further cooled to 46°C, Smectic S_C^{*} phase characterized by the formation of disclination line in the focal conic texture (Fig.2 b) was observed. The helical pitch values were determined by measuring the distance of the lines in a 70 μ m thick liquid crystal cell. Fig.3 presents the dependence of the helical pitch of polymer P-I on the temperature and molecular weight of polymer. At just below the S_A - S_C^{*} transition temperature, the helical pitch were not clear. The helical pitch increased with increasing molecular weight of P-I.

The x - ray diffraction data of polymer P-I were determined at room temperature. A sharp reflection has been observed at small angle region. A first-order reflection at 3.24nm and a second-order reflection at 1.94nm are corresponding to highly ordered smectic phase.

The photographs of texture of P-III are shown in Fig.4. Because of the highly melting viscosity of polymer, the texture of liquid crystalline polymer cannot enough develop. Fig.5 shows the temperature-dependent x-ray diffraction patterns obtained from powder samples of P-III at 95 and 65°C. Fig.5a presents diffuse reflection at wide angles, which is corresponding to lateral spacing of two mesogenic side groups, and a sharp reflection at about 3.55nm which corresponding to smectic layers. The results indicated that polymer P-III has Smectic A structure at 95°C. When the temperature was cooled to 65°C, the wide angle

reflection became very sharp (Fig.5b). The results show the formation of Smectic B phase. Polymer P-II ($n = 6$) didn't display liquid crystalline property.

Tab.2 Characterization of polymers

Polymers	Transition Temperature (°C)		Mn	Mw/Mn
	DSC	POM		
P - I	g -16 S _C * 46.4 S _A 81.2 I	S _C * 46 S _A 108 I	4.3×10^3	1.32
P - II	K 86 I	K 85 I	4.4×10^4	1.4
P - III	g 35 S _B 50.5 S _A 90.5 I	g 31 S _B ? S _A 95 I	1.2×10^4	1.4

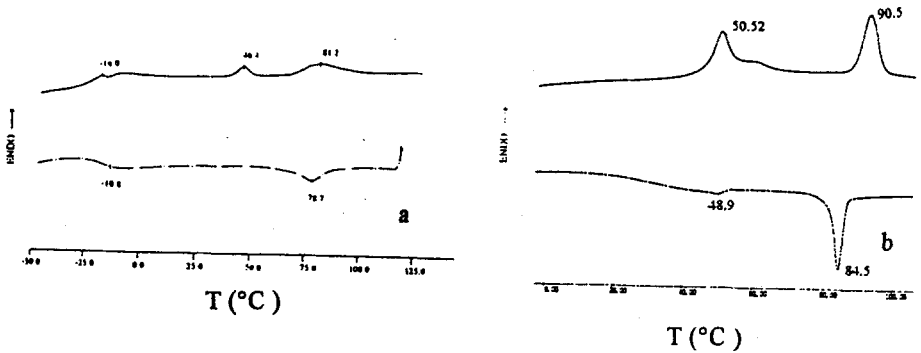


Fig.1 DSC curves of polymers (— heating , -●- cooling) a. P-I , b. P-III

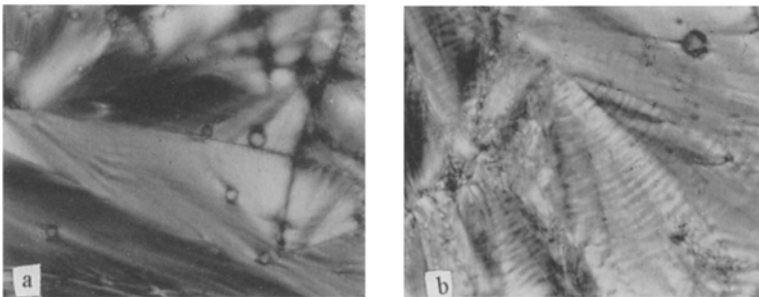


Fig. 2 Microphotographs of P-I
a. S_A texture on heating at 67°C , b. S_C* texture on cooling at 46°C

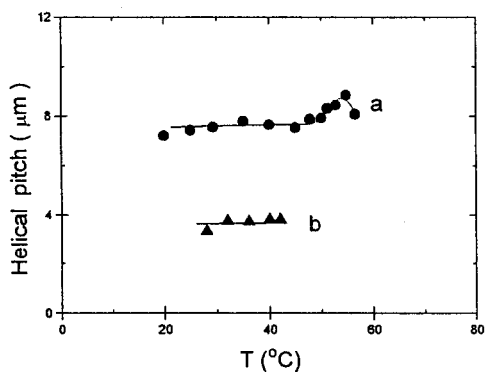


Fig. 3 Dependence of the helical pitch of P-I on Mn and temperature. The pitch values were measured in $70\mu\text{m}$ thick cells
 a. $Mn = 5881$, b. $Mn = 4291$

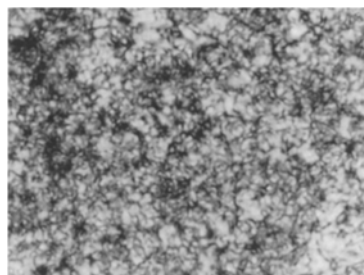


Fig. 4 Microphotograph of P-III at 65°C

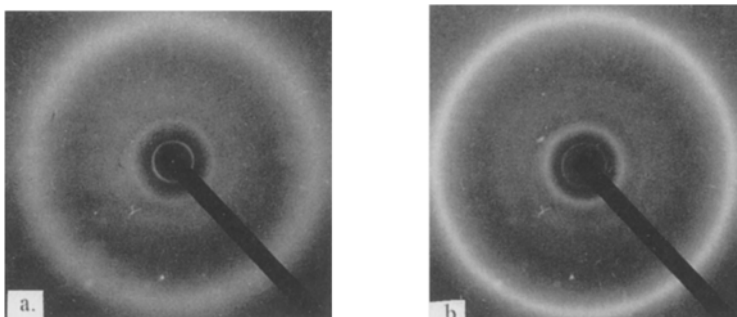


Fig. 5 X-ray diffraction patterns of P-III a. at 95°C b. at 65°C

In conclusion, two kinds of chiral side chain liquid crystalline polyacrylates were synthesized. The liquid crystalline behaviour of polymers was influenced by the chirality of end group and spacer length of side chain.

References

1. Nakamura T, Ueno T, and Tani C (1989) *Mol. Cryst. Liq. Cryst.* 169: 167
2. Chiellini E, Galli G, et al. (1993) *Makromol. Chem. Makromol. Symp.*, 69: 51
3. Zhang SF, Lien MQ (1992) *Chinese J. of Polym. Sci.*, 1992, 4: 36